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ADSORPTION OF ACETONITRILE AND ITS REACTION WITH OXYGEN ON TiO₂ – SUPPORTED Au – Rh BIMETALLIC CATALYSTS

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Abstract

The adsorption of acetonitrile and its surface reactions with oxygen on TiO₂-supported Au – Rh bimetallic catalysts were studied by FTIR and mass spectrometry at 300–673 K. The band due to CH₃CN on Lewis acid centres shifted to lower wavenumbers with the increase of the Rh content, which shows that the strength of Lewis acid sites weakens with the increase of the Rh content of the catalysts. CH₃CN, on the other hand, dissociates producing CN_(a) species. From the shift to higher wavenumbers of the band due to CN_(a), strengthening of the C – N bond with increasing Rh content has been established. During the heat treatments of the adsorbed CH₃CN layer, methylamine (CH₃NH₂) was detected in the gas phase, the amount of which depended on the composition of the catalysts. Dehydrogenation of the adsorbed acetonitrile also depends on the Rh content: the higher the Rh content of the sample, the lower the temperature of the first appearance of gaseous H₂, and the higher the amount of H₂ evolved. The presence of gaseous oxygen affects the formation of isocyanate (NCO) surface species only on 1% Au/TiO₂ and on 1% (0.75Au+0.25Rh)/TiO₂ catalysts.

Keywords: Acetonitrile adsorption, dissociation and dehydrogenation of acetonitrile, NCO formation

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INTRODUCTION

Acetonitrile (CH_3CN) and its isomer, methyl isocyanide (CH_3NC) have been relatively often used for determining the geometrical structure and bonding configuration on single crystal metal surfaces [1-9]. Their application is based on the fact that these compounds are isoelectronic with CO (the most frequently applied probe molecule). The probe molecule character of acetonitrile has also been explored in the study of the acid-base properties of supported catalysts [10-13].

Heterogeneous catalytic transformations of acetonitrile have rarely been investigated. It was found that CH_3CN adsorbed on Pt/SiO_2 could be – at least partly – hydrogenated [14]. The UV irradiation of CH_3CN adsorbed on TiO_2 in the presence of oxygen [15] led to the formation of H_2O , CO_2 , surface CO_3^{2-} and surface isocyanate (NCO). The formation of surface CH_3CONH_2 , $\eta^2(\text{N},\text{O})\text{-CH}_3\text{CONH}$, $\text{CH}_3\text{COO}_{(\text{a})}$, $\text{HCOO}_{(\text{a})}$, $\text{NCO}_{(\text{a})}$ and CN-containing species was observed, when the UV irradiation of CH_3CN adsorbed on TiO_2 was performed in the absence of oxygen [16].

The studies on the adsorption of CH_3CN and its reaction with O_2 on TiO_2 -supported Rh and Au [17,18], as well as on Al_2O_3 -supported noble metals [19] revealed that NCO can also be formed thermally. The formation of gas phase NH_3 on Al_2O_3 -supported noble metals and on Rh/ TiO_2 was considered as a proof for the rupture of the C-N bond in $\text{CN}_{(\text{a})}$ generated in the dissociation of acetonitrile on these surfaces. The detection of the formation of strong Lewis acid sites on TiO_2 and Al_2O_3 , on the other hand, has drawn the attention to the occurrence of an electron donation from TiO_2 and Al_2O_3 to the metal particles. This observation can be accepted as an experimental proof for the electronic interaction between the metal and the supports [17-19].

Their presumable multifunctionality has initiated a lot of studies on bimetallic catalysts. A very important task of these studies would be the characterization of these catalysts, as different, sometimes contradicting opinions have been appeared in the literature concerning the catalytic effect and mechanism of these catalysts [20]. Characterization of the Au-Rh bimetallic catalysts by CO adsorption has already been performed [21]. As a continuation, an attempt is made in this study to characterize the Au-Rh samples with the help of CH_3CN adsorption. Another aim of the present work is to investigate the effect of the presence of a second metal on the behavior of the original monometallic Au/ TiO_2 and Rh/ TiO_2 [17,18] in the catalytic reaction between CH_3CN and oxygen.

EXPERIMENTAL

TiO₂ was the product of Degussa (P25, 50 m²/g). The preparation of 1 w% Au/TiO₂ and 1 w% Rh/TiO₂ catalysts was described in details elsewhere [17–19]. The bimetallic Au – Rh catalysts with three different compositions were produced by impregnating TiO₂ with the mixtures of calculated volumes of HAuCl₄ and RhCl₃·x H₂O solutions to yield a 1 w.% metal content. The impregnated powders were dried in air at 383 K for 3 h. H₂ (99.999 %, Linde) and CH₃CN (99 %, Reanal) were used. The detailed experimental circumstances in FTIR and MS studies were published earlier [17–19].

RESULTS AND DISCUSSION

The C – N stretching region of the spectra detected during the adsorption of CH₃CN (1.33 Pa – 1.33 hPa) at 300 K on different catalysts is shown on Fig. 1. The assignments of these bands and of those appeared outside this region are collected in Table 1 and Table 2. Besides the band at 2291 – 2296 cm⁻¹ due to CH₃CN molecularly adsorbed on weak Lewis acid sites (Ti³⁺), a band at 2275 – 2283 cm⁻¹ attributed to physisorbed acetonitrile was observed in all spectra. The band at 2334 cm⁻¹ due to CH₃CN adsorbed on very strong Lewis acid sites [17–19] was detected only in the spectrum of 1 % Au/TiO₂ in 1.33 hPa CH₃CN. The band registered at 2186 – 2197 cm⁻¹ can be attributed to the CN vibration of CH₃CN molecules coordinated linearly through the lone electron pair of the N atom on Ti³⁺ or on metallic sites. The appearance of the bands in the range of 2170 – 2000 cm⁻¹ can be due to CN_(a) formed in the dissociation of acetonitrile on Ti³⁺ or metallic sites in different surface environments. The bands due to δ_{as} (CH₃) (1430 – 1464 cm⁻¹), δ_s (CH₃) (1354 – 1370 cm⁻¹) and ρ (CH₃) (1035 – 1053 cm⁻¹) of molecularly adsorbed CH₃CN can be clearly distinguished at lower wavenumbers. A band at 1698 – 1733 cm⁻¹ was registered on the surfaces investigated. The band observed at 1655 cm⁻¹ on Pt (111) [5] and at 1755 cm⁻¹ on Pd (111) (8) was attributed to η^2 (C,N) CH₃CN adsorbed species, and it was concluded that the above difference in the positions of the bands is the consequence of the different softening of the CN stretching mode: it was softened slightly less on Pd (111) than on Pt (111). Based on the above results obtained on single crystal surfaces, the band at 1698 – 1733 cm⁻¹ detected in our studies is assigned to η^2 (C,N) CH₃CN species formed on the surfaces studied here. The IR features observed at 2864 – 2876 cm⁻¹, 2760 – 2782 cm⁻¹ and 1112 – 1130 cm⁻¹ can be attributed to adsorbed CH₃NH₂ [17–18, 24–25]. The formation of methylamine might be connected with the participation of titania OH groups in the surface reactions. The appearance of the bands at 1637 – 1653 cm⁻¹ (δ (H₂O)), at 1565 – 1590 cm⁻¹ and 1519 – 1547 cm⁻¹ (possibly due to surface

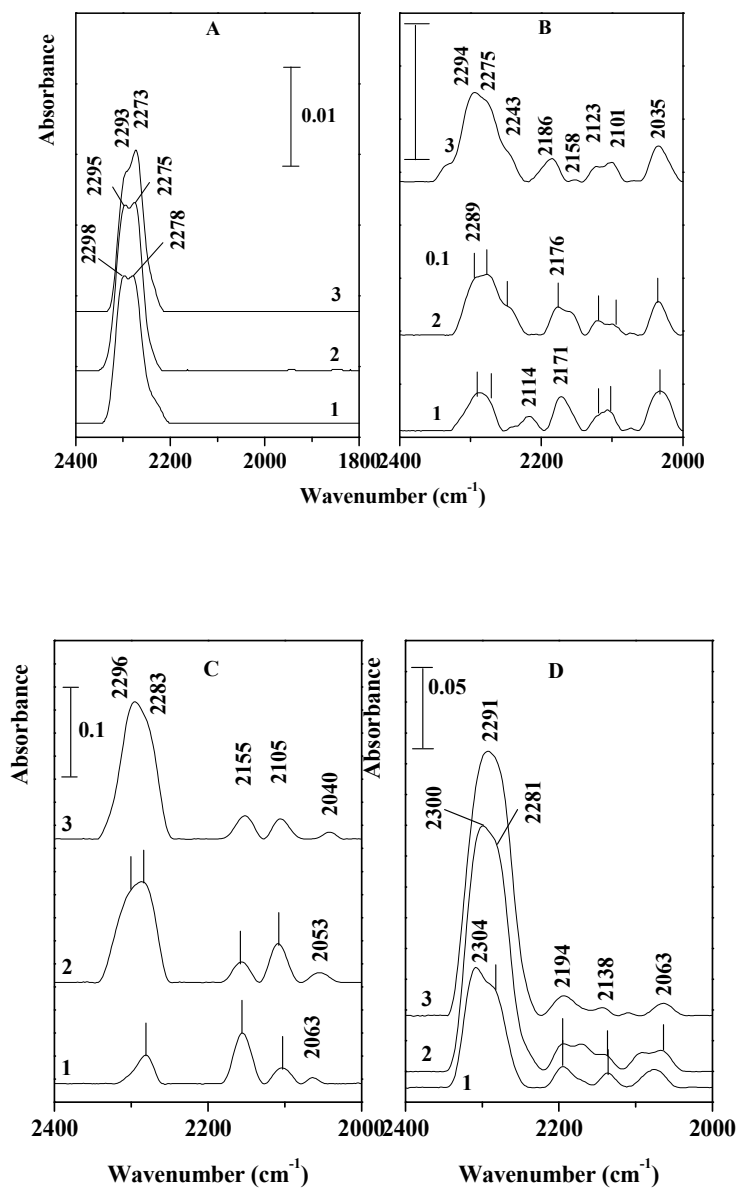


Fig. 1. The effect of the acetonitrile pressure on the spectra registered at 300 K on TiO_2 (A), on 1% Au/TiO_2 (B), on 1% $(0.5\text{Au}+0.5\text{Rh})/\text{TiO}_2$ (C) and on 1% Rh/TiO_2 (D): 1 – 1.33 Pa; 2 – 13.3 Pa and 3 – 1.33 hPa

carbonates) is the result of the surface oxidation of acetonitrile by the active oxygen of titania. We have not found any direct correlation between the positions, neither the integrated absorbance values of the above bands and the changes in the composition of the catalysts.

Table 1

Characteristic CH bands (in cm^{-1}) observed in CH_3CN adsorption on different surfaces

Assignment	Gas [22]	Pt (111) monolayer [4]	Pd (111) [8]	TiO_2^a	1 % Au/ TiO_2^a	1%(0.75Au +0.25Rh) / TiO_2^a	1%(0.5Au +0.5Rh) / TiO_2^a	1%(0.25Au +0.75Rh) / TiO_2^a	1% Rh/ TiO_2^a
$\nu_{\text{as}}(\text{CH})$	3009	3005		2999	3000	3029	3028	3018	3012
$\nu_{\text{s}}(\text{CH})$	2954	2960		2960	2968	2977	2973	2987	2986
$\delta_{\text{as}}(\text{CH}_3)$	1448	1435	1447, 1410	1456	1449	1437	1430	1464	1453
$\delta_{\text{s}}(\text{CH}_3)$	1385	1375	1371	1370	1355	1367	1365	1354	1367
$\rho(\text{CH}_3)$	1041	1060	1040	1053	1036	1035	1052	1035	1043

^a This work

In the following experiments the stability of the adsorbed CH_3CN layer (produced on the catalysts by the adsorption of 1.33 hPa CH_3CN at 300 K for 15 minutes) was studied. For this purpose, the samples with adsorbed CH_3CN layer on their surfaces were heated under evacuation to different temperatures (in 50 K steps), and were kept at the given temperature for 1 minute; after this treatment the samples were cooled down to room temperature and the IR spectra were always taken at 300 K.

On TiO_2 the intensity of the 2268 cm^{-1} band decreased, while that of the bands at 2165 and 2127 cm^{-1} slightly increased with the increase of the temperature. At and above 373 K a band at $2200\text{--}2216\text{ cm}^{-1}$ due to Ti – NCO [26 – 28] appeared in the spectra. On monometallic Au/ TiO_2 sample the surface concentration of CH_3CN adsorbed on weak Lewis acid sites (2282 cm^{-1}) was higher than that of CH_3CN adsorbed on strong Lewis acid centres (2320 cm^{-1}) at 300 K. At 300 – 573 K, a band due to Ti – NCO (2213 cm^{-1}) was observable in the spectra. On the spectra of 1% Rh/ TiO_2 , the intensity of the 2316 cm^{-1} band (CH_3CN adsorbed on strong Lewis acid centres) was higher than that of the band due to CH_3CN adsorbed on weak Lewis acid sites (2282 cm^{-1}). No band due to Ti – NCO surface species was detected on the Rh/ TiO_2 catalyst. On all TiO_2 -supported Au–Rh bimetallic catalysts the relatively intense 2293 cm^{-1} band (observed after the evacuation at 300 K) was split into the bands at 2307 and 2288 cm^{-1} at 373 K, the intensities of which decreased in a different way

with the further increase of the temperature; they disappeared above 573 K. At 300 – 473 K a small band due to Ti – NCO was observed.

Table 2

Characteristic CN bands (in cm^{-1}) observed in CH_3CN adsorption on different surfaces

Assignment	Gas [22]	H/beta zeolites [11]	Pt (111) [4]	Pd (111) [8]	TiO_2^a	1 % Au/ TiO_2^a	1%(0.75Au +0.25Rh) / TiO_2^a	1%(0.5Au +0.5Rh) / TiO_2^a	1%(0.25Au +0.75Rh) / TiO_2^a	1% Rh/ TiO_2^a
$\nu(\text{CN})$ in CH_3CN on very strong Al- Lewis sites										
$\nu(\text{CN})$ in CH_3CN on strong Al- Lewis sites		2325- -2330								
$\nu(\text{CN})$ in CH_3CN on weak Al-Lewis sites		2310- -2315			2295	2291	2295	2296	2299	2291
$\nu(\text{CN})$ in free molecular CH_3CN	2267									
$\nu(\text{Ti-CN})$					2195	2186	2198		2198	2194
$\nu(\text{M-CN})$						2122, 2101, 2035	2158,2123 2060,2028	2155,2105 2063- 2046	2159 2107,2053	2138 2076- 2063
$\eta^2(\text{C,N}) \text{CH}_3\text{CN}$			1615	1755	1719	1704	1733	1713	1698	1717

^a This work

The bands due to $\nu_s(\text{CH}_3)$, $\delta_{\text{as}}(\text{CH}_3)$, $\delta_s(\text{CH}_3)$ and $\rho(\text{CH}_3)$ of adsorbed CH_3CN (not shown) changed parallel with the above bands due to $\nu(\text{CN})$ in adsorbed CH_3CN . Interestingly, the bands due to $\eta^2(\text{C,N}) \text{CH}_3\text{CN}_{(\text{a})}$ disappeared at by 100 – 150 K higher temperature than that due to $\text{CH}_3\text{CN}_{(\text{a})}$ on Lewis sites. Bands with small intensity due to adsorbed methylamine (2864 – 2876, 2760 – 2782 and 1112 – 1130 cm^{-1}) were observed up to 573 – 623 K. No other bands attributable to newly formed surface species could be registered.

During the heat treatments of the adsorbed CH_3CN layer the changes in the gas phase composition were monitored using mass spectrometry, and the data for some gas phase products are depicted in Fig. 2.

There was no acetonitrile desorption from TiO_2 . The peak maximum of CH_3CN desorption was observed at 423 – 473 K from mono- and bimetallic samples. Methylamine (CH_3NH_2) desorbed in the highest amount from TiO_2 ($T_{\text{max}} = 423 \text{ K}$). CH_3NH_2 desorption from mono- and bimetallic catalysts shows a peak maximum at 473 K. The amounts of desorbed methylamine were smaller

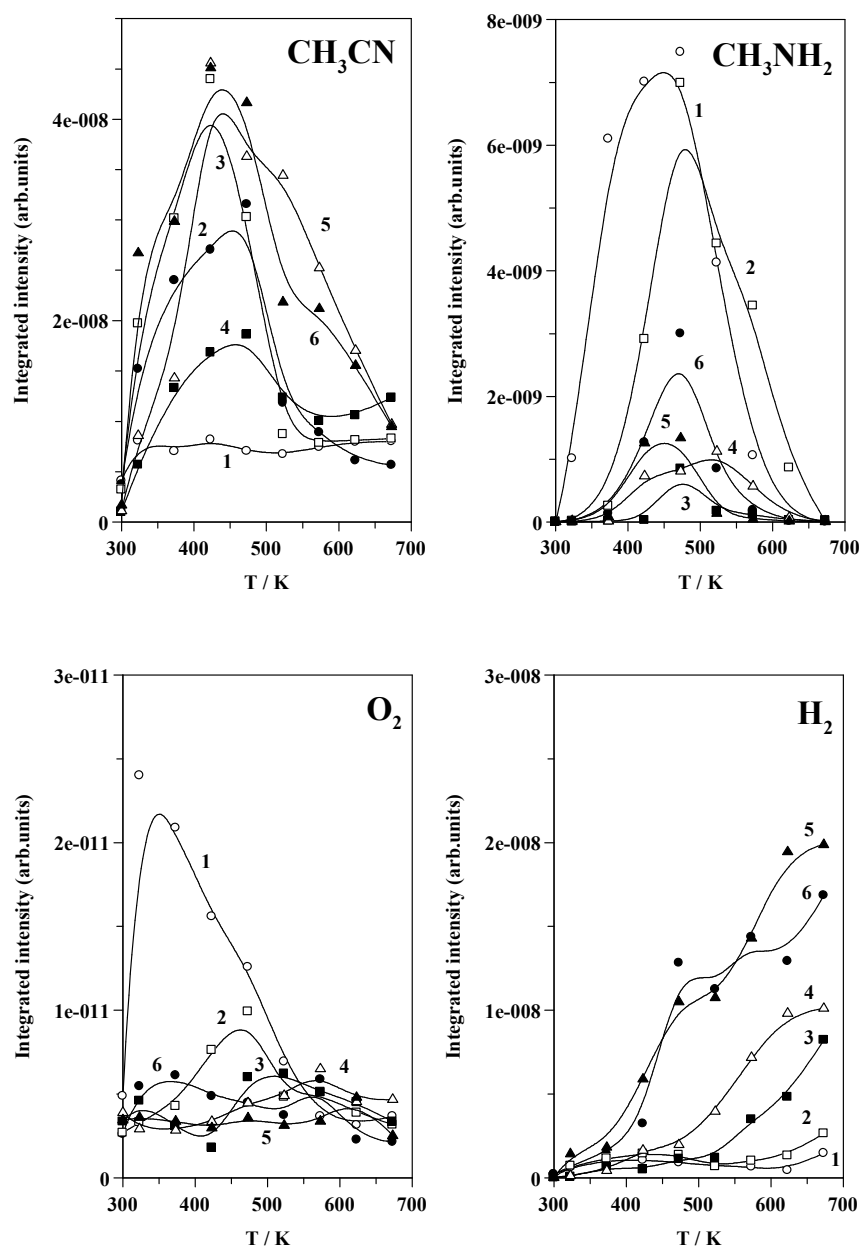


Fig. 2. Mass spectroscopic detection of gas phase products formed during the vacuum heat treatments of adsorbed CH₃CN layer: 1 – TiO₂; 2 – 1% Au/TiO₂; 3 – 1% (0.75Au+0.25Rh)/TiO₂; 4 – 1% (0.5Au+0.5Rh)/TiO₂; 5 – 1% (0.25Au+0.75Rh)/TiO₂ and 6 – 1% Rh/TiO₂

in the cases of bimetallic samples. O_2 desorption was observed only from TiO_2 ($T_{max} = 323$ K) and from 1% Au/TiO_2 ($T_{max} = 473$ K). The temperature of the first appearance of hydrogen in the gas phase and the amount of H_2 evolved depended on the rhodium content of the catalysts: the lower the Rh content, the higher the temperature of the first appearance of H_2 , and the smaller its amount in the gas phase. No hydrogen desorption was observed from 1% Au/TiO_2 and TiO_2 samples. The highest amount of CH_4 was formed on 1% Rh/TiO_2 monometallic catalyst ($T_{max} = 473$ K). With the decrease of the Rh content, the amount of methane formed decreased and a peak maximum at 600 – 673 K developed at the expense of the peak at $T_{max} = 473$ K. The appearance of ethylene in the gas phase can be correlated with that of methylamine. Both methylamine and ethylene desorptions show a peak maximum at 473 K and their amounts change parallel as a function of the catalyst composition. A small amount of gas phase ammonia could be detected on 1% Rh/TiO_2 ; no NH_3 formation was observed on any other samples.

The stability of adsorbed CH_3CN layer was also studied in the presence of oxygen. In these experiments no bands in the 2400 – 2000 cm^{-1} range appeared in the spectra of TiO_2 above 473 K. On the spectra of monometallic 1% Au/TiO_2 and 1% Rh/TiO_2 catalysts the bands in the CN region were registered even after heat treatment at 673 K. A small band around 2210 cm^{-1} (due to Ti – NCO [26 – 28]) appeared already at 300 K in the spectra of Au/TiO_2 , and at and above 473 K in the spectra of Rh/TiO_2 in O_2 . The Ti – NCO band with small intensity was detected already at 300 K in the spectra of bimetallic catalysts very probably due to the presence of gold.

Next the interactions of 1.33 hPa CH_3CN and that of 1.33 hPa CH_3CN + 13.3 Pa O_2 gas mixture were investigated isothermally at 300, 373, 473 and 573 K for 60 minutes. In these experiments the IR spectra were taken at the reaction temperature, and the spectra of the reduced catalyst and the gas phase were subtracted from the spectra registered in the reacting gas. Changes in the gas phase composition were simultaneously followed by mass spectrometry. Changes both in the IR spectra and in the gas phase composition started to occur at 373 K. At and above this temperature the intensities of the IR bands decreased and parallel with the small decrease in the amount of CH_3CN , the concentration of the reaction products slightly increased in the gas phase.

Differences in the C – N range of the IR spectra obtained in the CH_3CN adsorption on different catalysts became more obvious at 473 K (Fig. 3). Bands at 2359 cm^{-1} (due to adsorbed CO_2), at 2322 cm^{-1} (CH_3CN adsorbed on very strong Lewis acid sites), at 2218 cm^{-1} (Ti – NCO) and at 2117 cm^{-1} ($CN_{(a)}$) appeared in the spectrum of TiO_2 . In the spectrum of 1% Au/TiO_2 these bands were registered at 2359, 2315, 2218 and 2120 cm^{-1} . With the increase of the Rh content of the catalysts, further continuous shift to lower wavenumbers occurred in the position of the band due to CH_3CN adsorbed on very strong Lewis acid

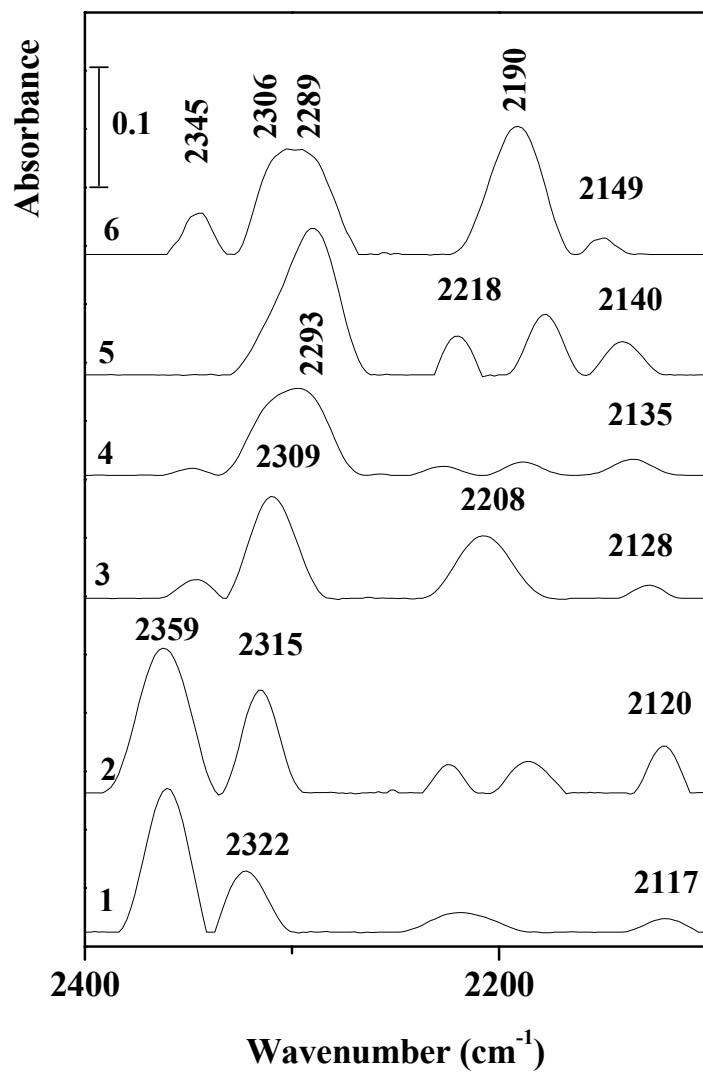


Fig. 3. 2400-2100 cm^{-1} region of the spectra registered in 13.3 hPa CH_3CN at 473 K after 60 min: 1 – TiO_2 ; 2 – 1% Au/TiO_2 ; 3 – 1% (0.75Au+0.25Rh)/ TiO_2 ; 4 – 1% (0.5Au+0.5Rh)/ TiO_2 ; 5 – 1% (0.25Au+0.75Rh)/ TiO_2 and 6 – 1% Rh/ TiO_2

sites; on catalysts having the highest amount Rh a band due to CH_3CN adsorbed on weak Lewis acid centres ($2293 - 2289 \text{ cm}^{-1}$) also appeared. In our previous works a band attributed to acetonitrile coordinated on strong Lewis acid centres has been detected on both Au/TiO_2 (18) and Rh/TiO_2 catalysts (17). On TiO_2 only the band due to acetonitrile adsorbed on weak Lewis acid centres has been registered [17-18]. The formation of strong Lewis acid sites was connected with the presence of metals (Au and Rh), and it was interpreted as a consequence of the electron donation of Ti-cations on the surface to monometallic (Au and Rh) particles. The direction of the electron transfer is governed by the work function values of reduced TiO_2 ($\Delta\phi=4.8 \text{ eV}$) and that of the metals ($\Delta\phi_{\text{Au}}=5.38 \text{ eV}$ and $\Delta\phi_{\text{Rh}}=4.98 \text{ eV}$). These values suggest that the electron may flow from titania to the metals. This electron donation would increase the electron withdrawing power of the cationic sites (*i.e.* the strength of Lewis acidity of Ti-cations). The shift observed here in the position of the band attributed to CH_3CN adsorbed on very strong Lewis acid sites with the increase of Rh content of the catalysts refers to the decrease in the electron withdrawing power of the Ti-cationic sites. The band due to $\text{CN}_{(\text{a})}$ was shifted in the opposite direction: with the increase of Rh content this band shifted to higher wavenumbers. From these data it can be concluded that the increase of Rh content of the catalysts weakens the acid strength of Lewis centres, which is probably due to less electron donation from titania to the metal particles. This would lead to less electron back donation of metal particles to the antibonding orbital of the bond in $\text{CN}_{(\text{a})}$, consequently the bond in $\text{CN}_{(\text{a})}$ became stronger with increasing Rh content, thus the band due to $\text{CN}_{(\text{a})}$ shifts to higher wavenumbers. The above findings permit the conclusion that the bands due to the adsorption of acetonitrile and its derivative (CN) can be used for the characterization of dual functions (strength of Lewis acid sites and the electron density on the metal centres) of the bimetallic catalysts.

The presence of oxygen enhanced the formation of Ti – NCO species on 1% Au/TiO_2 and on 1% $(0.75\text{Au}+0.25\text{Rh})/\text{TiO}_2$ catalysts. Interestingly, the presence of oxygen did not change the extent of Ti – NCO production on 1% Rh/TiO_2 , 1% $(0.5\text{Au}+0.5\text{Rh})/\text{TiO}_2$, 1% $(0.25\text{Au}+0.75\text{Rh})/\text{TiO}_2$ and TiO_2 . We think that the dissociation of CH_3CN resulting in $\text{CN}_{(\text{a})}$ species and the consecutive oxidation of $\text{CN}_{(\text{a})}$ (by lattice oxygen or more effectively by gaseous oxygen) would lead to the formation of NCO. After its formation mainly on the metallic component of the catalysts, NCO migrates quickly to the support and localizes there [26 – 28].

CONCLUSIONS

1. Acetonitrile bonds molecularly to the studied surfaces through the lone pair electrons of its nitrogen to strong and weak Lewis acid sites of the support and through both carbon and nitrogen atoms of its CN (η^2 (C,N) species). The strength of Lewis acid sites weakens with the increase of the Rh content of the catalysts.

2. Acetonitrile adsorbed on TiO₂ and on monometallic samples can be hydrogenated into methylamine. The formation of CH₃NH₂ is greatly suppressed on bimetallic catalysts.

3. Acetonitrile dissociates producing CN_(a). The bond strength of CN_(a) becomes stronger with increasing Rh content of the catalysts.

4. Dehydrogenation of adsorbed CH₃CN depends linearly on the Rh content of the samples. No dehydrogenation of CH₃CN_(a) proceeds on Au/TiO₂ and on TiO₂.

5. Gaseous oxygen greatly enhances the formation of Ti – NCO species on 1% Au/TiO₂ and on 1% (0.75Au+0.25Rh)/TiO₂ catalysts; on bimetallic samples with lower Au content, as well as on Rh/TiO₂ and TiO₂ gaseous O₂ did not affect the surface concentration of Ti – NCO species.

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